



Hydrogen production by ethanol steam reforming over Rh nanoparticles supported on lanthana/silica systems



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ABSTRACT

The aim of the present work was to investigate Rh nanoparticle catalysts supported on La₂O₃-SiO₂, with different contents of La₂O₃, in the ethanol steam reforming reaction. The size of Rh particles was determined by both XPS, applying the Davis model, and CO chemisorption measurements. Particle sizes between 1.2 and 3 nm were estimated with these techniques. The catalyst with 15 wt.% of La₂O₃ was the most stable one under the different reaction conditions under study, i.e. 773 K and water to ethanol molar ratios of 3 and 5. In order to explain the deactivation observed in the other catalysts, the samples used in the reaction were characterized by XPS, TEM and in situ Raman spectroscopy. The TEM results allowed a direct visualization of the carbon deposits that presented different degrees of catalyst coverage. The surface of the most stable catalyst was not fully covered by carbon while the Rh/La₂O₃(40)-SiO₂ sample, which deactivated partially, exhibited a carbon layer uniformly distributed over the surface. The oxidation of the carbon deposits was analyzed using in situ Raman spectroscopy. Results were in agreement with those obtained by TEM microscopy. DRIFTS experiments under reaction conditions suggested that the direct decomposition of ethoxy species would produce hydrogen, CO, and CH_x species, which could result in carbon formation.

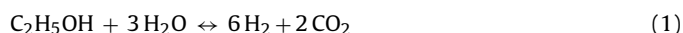
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1. Introduction

The world's energy matrix is primarily based on fossil-derived fuels which emit high levels of greenhouse gases [1], thus intensifying the natural greenhouse effect and causing damaging environmental impact. A diversification of the energy matrix including other cleaner energy sources such as photovoltaic, solar, or geothermal energy and renewables – wind, biomass, oceanic waves and tides – would reduce the negative impact on the environment and on human health and contribute to sustainable energy access.

In this context, hydrogen as an energy carrier could play a central role due to its waste-free combustion, high energy mass density and the vast variety of raw materials that can be used in its production. The prospects of hydrogen as an energy vector is strongly related to the development of fuel cells, which can directly generate electricity from hydrogen electrochemical combustion. PEM

fuel cells are used for transport applications as well as for stationary and portable applications. Among the different sources of hydrogen, ethanol is considered an excellent choice due to its almost close carbon cycle of production, low toxicity (compared with methanol, for example) and aggregate state under normal conditions. Ethanol steam reforming (ESR) is a global reaction that produces 6 mol of hydrogen per mol of ethanol.



Depending on the catalyst used and the operating conditions employed, several reactions may occur in parallel such as ethanol decomposition, dehydrogenation and dehydration, methane steam reforming, water gas shift (WGS) and hydrogenation reactions; all these parallel reactions produce acetaldehyde, hydrogen, methane, carbon oxides and ethylene [2].

One of the major problems in ethanol steam reforming is the formation of coke on the catalyst surface, which may take place via several processes, e.g. the Boudouard reaction, methane decomposition and polymerization of ethylene produced by dehydration of ethanol.

Increasing the reaction temperature leads to an increase in ethanol conversion. This is accompanied by a simultaneous

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decrease in the selectivities of acetaldehyde, acetone, and ethylene and an increase in H₂, CO, CO₂, and CH₄ selectivities.

Numerous catalysts based on noble metals such as rhodium, platinum, iridium, palladium and ruthenium as well as non-noble metals, such as cobalt, nickel and copper have been studied for the steam reforming of ethanol [3–6]. Among noble metals, several studies have shown that rhodium based catalysts are the most active and selective ones for hydrogen production [7].

Furthermore, the support may influence the catalytic properties of the metals for the ethanol steam reforming. The use of basic supports such as magnesium oxide [8] and lanthanum oxide [9] has proved to be a promising alternative to minimize coke deposition. However, their low specific surface areas lead to a low metal dispersion, in this way decreasing the catalyst performance [7]. On the other hand, acid supports such as gamma alumina favor the dehydration of ethanol leading to an increase in the production of ethylene, which is pointed out as the major precursor of coke in ethanol steam reforming [10].

The performance of several rhodium based catalysts has recently been reported. Noronha and coworkers [11] studied the performance of Rh catalysts supported on CeO₂ with different surface areas. These authors found that the catalyst with higher surface area showed a stability of 28 h in the reaction ($T = 773$ K and H₂O/ethanol = 3), while the catalyst with lower surface area showed deactivation after 6 h on stream. This difference was attributed to the greater oxygen availability from the support which favors the removal of carbonaceous deposits.

Roh et al. [12] studied Rh catalysts supported on several supports such as Al₂O₃, MgAlO₄, ZrO₂, CeO₂–ZrO₂. They found that the Rh/CeO₂–ZrO₂ catalyst exhibited the highest H₂ yield at 723 K, assigned to the high O₂ storage capacity of CeO₂–ZrO₂. Note that these samples have a Rh metal load of 2 wt.%.

Lin and coworkers [13] studied the role of acid sites on the catalytic steam reforming of ethanol using Rh catalysts supported on different types of ZrO₂. In order to modify the acid and basic properties of the support, the authors added small amounts of La₂O₃, CeO₂ and Al₂O₃. They found that at low temperature (573 K), the Rh catalyst based on the La promoted ZrO₂ support with two types of acid sites was more active, while above 723 K all the catalysts exhibited a similar catalytic activity.

A kinetic study of the ethanol steam reforming in the range of 773–873 K was carried out on a Rh catalyst supported on a spinel structure (MgAl₂O₄/Al₂O₃) [14]. From the kinetic analysis, the authors concluded that the system can be described by three reactions, i.e. ethanol decomposition, methane steam reforming and water gas shift.

In previous publications [15,16], we reported the synthesis of the catalyst containing a low Rh content (0.6 wt.%) using La₂O₃–SiO₂ with 27 wt.% of La₂O₃ as support. The catalyst

presented a high metal dispersion, about 79%, and was active and stable for the dry reforming of methane [17] and the water gas shift (WGS) reaction [18]. The formation of an amorphous lanthanum disilicate phase yielded a proper metal–support interaction that led to a high metal dispersion and high methane reaction rates.

The purpose of this work was to apply Rh-based catalysts supported on La₂O₃–SiO₂ binary supports to the steam reforming of ethanol for hydrogen production. In order to increase the stability of the catalysts under severe reaction conditions, we explored different lanthanum oxide contents as well as the addition of small amounts of cerium to the catalyst. The average metal particle size was determined by CO chemisorption measurements and by applying the XPS Davis model, finding a good agreement between both techniques. The deposition of graphitic carbon was studied by XPS, in situ Raman spectroscopy and TEM analysis.

2. Experimental

2.1. Catalyst preparation

The catalyst and the supports were prepared by the incipient wetness impregnation technique. SiO₂ (Aerosil 200, calcined at 1173 K) was impregnated using La(NO₃)₃·6H₂O, RhCl₃·6H₂O and Ce(NO₃)₃·6H₂O as precursors. All supports and catalysts were calcined at 823 K for 6 h in air flow.

The Rhodium content of all catalysts was 0.6 wt.%. On the other hand, the amount of lanthanum in the support was varied; three different compositions were prepared 15, 27 and 40 wt.% of La₂O₃ (La₂O₃(x)–SiO₂). The support surface area was measured after calcination at 823 K. The values were 188, 143 and 88 m² g^{−1} for the supports with 15, 27 and 40 wt.% of La₂O₃, respectively. The addition of 2% of cerium to both the catalyst and the support with 15 wt.% of lanthanum was also studied. In this case, the surface area was equal to 123 m² g^{−1}.

The name of the catalyst denotes the species present in that catalyst and, from right to left, the order in which they were added. In the case of lanthanum oxide, the content is also indicated between brackets (see Table 1).

2.2. Catalytic tests

The catalysts were evaluated in a fixed-bed reactor using 20 mg of catalyst diluted in 60 mg of inert quartz (Mesh 100) in order to avoid internal thermal gradients. The catalysts were heated in Ar flow to 773 K in 1 h and then they were reduced in pure hydrogen flow for 2 h, at the same temperature. After that, the water–ethanol mixture was fed to the system by a syringe pump, mixed with Ar and evaporated in an evaporator at 493 K. The mixture was prepared by weight, using anhydrous alcohol and deionized water.

Table 1
Binding energies and surface atomic compositions (%) of reduced and used catalysts determined by XPS.

Catalyst	Rh 3d _{5/2} ^a	La 3d _{5/2} ^a	Rh ^b	La ^b	Si ^b	Ce ^b	Rh/La	Rh ^c	La ^c	Rh/La ^c
Rh/La ₂ O ₃ (15)–SiO ₂	306.8(2.8)	835.2(3.4)	0.11	2.0	33.00	–	0.055	0.10	2.06	0.063
Used	307.3(3.1)	834.9(3.5)	0.16	1.1	25.8	–	0.15	–	–	–
Rh/La ₂ O ₃ (27)–SiO ₂	307.1(3.1)	834.9(3.5)	0.18	3.1	32.25	–	0.058	0.14	4.08	0.034
Rh/La ₂ O ₃ (40)–SiO ₂	306.7(2.7)	835.0(3.4)	0.24	4.3	32.93	–	0.056	0.16	6.63	0.024
Used	308.4(3.5)	835.2(3.1)	0.30	5.6	24.8	–	0.054	–	–	–
Rh/CeO ₂ –La ₂ O ₃ (15)–SiO ₂	307.1(3.4)	835.1(3.8)	0.17	2.3	32.84	0.65	0.073	0.13	2.04	0.063
Calcined	309.1(2.7)	834.9(3.1)	0.12	1.03	28.1	0.50	0.12	–	–	–
Used	308.6(2.5)	834.8(3.1)	0.07	1.43	26.8	–	0.048	–	–	–
CeO ₂ –Rh/La ₂ O ₃ (15)–SiO ₂	306.8(3.1)	835.0(3.5)	0.13	2.0	32.79	0.51	0.065	0.13	2.04	0.063

^a For all fresh samples the binding energy for C 1s was 284.6 ± 0.1 eV and for Si 2s was 153.9 ± 0.1 eV. FWHM are shown between parentheses (eV). Satellite/main peak splits for La 3d_{5/2} = 3.7 eV.

^b Surface atomic compositions (%) determined by the peak intensity of Rh, La, Si and O.

^c Nominal atomic composition of the catalysts.

Two different water/ethanol molar ratios were prepared, 3 and 5, and the molar ethanol contents in each reactant flow were 2.5 and 2.0%, respectively. The inert gas flow rate was 60 mL·min⁻¹. The feed and product flows were analyzed with a Shimadzu GC-2014 gas chromatograph equipped with a TCD detector and a 10-meter long Haysep D[®] packed column. All pipes and valves were maintained at 473 K in order to avoid reactant and product condensation. The absence of homogeneous reaction was verified at 773 K.

Ethanol conversion (X_{ethanol}), space velocity (W/F) and product composition (y_i) were defined by the following equations:

$$X_{\text{ethanol}}(\%) = \frac{100 \times (F_{\text{ethanol}}^{\text{in}} - F_{\text{ethanol}}^{\text{out}})}{F_{\text{ethanol}}^{\text{in}}} \quad (2)$$

$$\frac{W}{F} = \frac{m_{\text{catalyst}}}{F_{\text{Total}}^{\text{in}}} \quad (3)$$

$$y_i(\%) = \frac{100 \times F_i}{\sum_j F_j} \quad (4)$$

where $F_{\text{ethanol}}^{\text{in}}$ and $F_{\text{ethanol}}^{\text{out}}$ are the molar flow of ethanol at the inlet and outlet, respectively, W is the catalyst mass in grams (g) and $F_{\text{Total}}^{\text{in}}$ is the total volume flow in the inlet (including Ar) expressed in liters at standard temperature and pressure per hour (Lh⁻¹). It is important to note that the product composition excludes water, ethanol and argon species from the calculations.

2.3. Thermodynamic calculations

Thermodynamic equilibrium compositions were calculated by Gibbs free energy minimization using COCO simulator software [19]. Peng Robinson was used as a property package and the reaction conditions were the same as the ones described above. The thermodynamic calculations (not shown) were compared with those reported in the literature [20] and a very small difference between the values was observed, less than 2%, taking into account that the model used here only includes species that can be determined by chromatography (H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆O, H₂O and C₂H₅OH) and that the calculations performed by Díaz Alvarado et al. [20] also considered different kinds of carbonaceous deposits. Since our calculations did not take into account the possibility of carbon formation, an additional online software [21] was used, which is able to predict the formation of a new carbonaceous phase. As a result, the difference between the composition values calculated with each software were always less than 1.4% and no carbon formation was predicted under experimental conditions.

In addition, several thermodynamic studies [22] found that carbon formation depends on both the reaction temperature and the water to ethanol ratio. For water to ethanol molar ratios higher than 3, carbon is not formed at reaction temperatures above 600 K.

2.4. Characterization

2.4.1. X-ray diffraction (XRD)

The XRD patterns of the calcined samples were obtained with an XD-D1 Shimadzu instrument, using Cu-K α radiation at 30 kV and 40 mA. The scan rate was 1° min⁻¹ for values between $2\theta = 10^\circ$ and 70° .

2.4.2. Metal dispersion

The metal dispersion of the fresh catalyst was determined by static equilibrium adsorption of CO at 298 K in a conventional vacuum system. The volumetric adsorption measurements were carried out in a conventional glass vacuum apparatus. About 200 mg of the catalyst were placed in a quartz cell, degassed for 1 h at reduction temperature, then reduced in H₂ flux at 773 K

for 1 h and evacuated at the same temperature for 1 h. Next, the sample was cooled under vacuum to the adsorption temperature. Adsorption isotherms were measured at 298 K, with exposure times varying between 10 min and 4 h. After the first isotherm was recorded, the adsorption cell was outgassed for 10 min at adsorption temperature and a second isotherm was measured. The amount of irreversibly adsorbed CO was determined by assessing the difference between the isotherms. The pressure range of the isotherms was 0.132–2.03 kPa.

A relationship between metal dispersion and the average particle size for several metals was reported in the literature [23] through Eq. (5). Spherical metal particles and equal portions of the three low-index planes (1 1 1), (100) and (1 1 0) on the polycrystalline surface of a fcc metal were assumed as follows:

$$d \text{ [nm]} = \frac{v_m \times 6}{a_m \times D} \quad (5)$$

where d is the average particle diameter, D is the metallic dispersion, v_m is the volume occupied by an atom in a bulk metal and a_m is the area occupied by a surface atom. In this case, Rh parameters [23] were used, a_m : 7.58×10^{-2} nm² and v_m : 1.378×10^{-2} nm³.

2.4.3. X-ray photoelectron spectroscopy (XPS)

The XPS measurements were carried out using a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with pass energy of 30 eV; a Mg-K α X-ray source was operated at 200 W and 12 kV. The XPS analyses of fresh catalysts were performed after a reduction treatment in H₂ flow; first a treatment in a fixed bed reactor at 773 K for 2 h and then, an in-situ treatment for 10 min at 673 K in a H₂/Ar stream, carried out in the reaction chamber of the spectrometer. The spectral regions corresponding to Ce 3d, La 3d, C 1s, O 1s, Si 2s and Rh 3d core levels and the Rh M₄₅VV Auger peak were recorded for each sample.

The data treatment was performed with the Casa XPS program (Casa Software Ltd, UK). The peak areas were determined by integration employing a Shirley-type background. Peaks were considered to be a mixture of Gaussian and Lorentzian functions in a 70/30 ratio. For the quantification of the elements, sensitivity factors provided by the manufacturer were used.

The Davis model was applied [24] to estimate Rh particle size. This method is based on the intensity ratio between two peaks of the same dispersed phase coming from two different electronic levels, which are sufficiently separated in energy. The two core levels used were Rh 3d with a binding energy approximately at 307 eV and the Auger Rh M₄₅VV with a kinetic energy of 301 eV. The main requisite parameters for applying the model were the peak areas and the inelastic mean free path (IMFP, λ). The IMFPs used in this work were calculated with the Tougaard Quases-IMFP-TPP2M program [25]. The intensity ratio of two dispersed phase core levels is given as:

$$\frac{I_1(d)}{I_2(d)} = \frac{\sigma_1 T_1 \lambda_1 \beta(d, \lambda_1)}{\sigma_2 T_2 \lambda_2 \beta(d, \lambda_2)} \quad (6)$$

where σ is the photoemission cross-section, T is an instrumental transmission function that reflects the basic detection efficiency, λ is the IMFP of the primary photoelectron and β is the attenuation factor which is characteristic of the particle shape and photoelectron attenuation length. This attenuation factor may be derived for different particle shapes using the relation given by Davis [24]. Assuming cubic dispersed phase morphology, $\beta(d, \lambda)$ is given by:

$$\beta(d, \lambda) = 1 - \left(\frac{\lambda}{\sqrt{2}d} \right) \left[1 - \exp \left(-\frac{\sqrt{2}d}{\lambda} \right) \right] \quad (7)$$

where d is the particle size and could be obtained by iteration. More details about the calculations can be obtained from the original work [24]. A metallic Rh powder was used as reference material.

2.4.4. Temperature-programmed oxidation (TPO)

The catalysts, used during 24 h in the steam reforming of ethanol at 773 K, with a water to ethanol molar ratio of 5 and a space velocity of $4.9 \times 10^{-3} \text{ g h L}^{-1}$, were exposed to a mixture of 20% O_2 in Ar at increased temperatures, from 293 to 1073 K, with a rate of 10 K min^{-1} . The gas flow rate was 30 ml min^{-1} and the reactor outlet was analyzed by a Balzers ThermoStar Mass Spectrometer, which has a carbon dioxide detection limit of $1.5 \mu\text{mol}$.

2.4.5. DRIFT and laser Raman spectroscopy (LRS)

Diffuse reflectance infrared Fourier-transform spectroscopy were obtained using a Smiths Illuminator II JY spectrometer. The spectra were obtained with a resolution of 4 cm^{-1} and 128 scans; the reference spectrum for each experiment was taken when the catalyst was under He flow, after reduction and before the introduction of reactive gases.

The Raman spectra were recorded using a LabRam spectrometer (Horiba-Jobin-Yvon) coupled to an Olympus confocal microscope (a $100\times$ objective lens was used for simultaneous illumination and collection), equipped with a CCD detector cooled to about 200 K using the Peltier effect. The excitation wavelength was in all cases 532 nm (diode-pumped solid-state laser). The laser power was set at 30 mW.

In situ LRS and DRIFTS measurements were performed on a Linkam high temperature cell. The catalyst (15 mg) was loaded in powder and the feed flowed through the samples. The feed mixtures were prepared in a flow system built for this purpose.

In the high temperature cell, different treatments were carried out as follows:

- The catalysts were exposed to 5% H_2/Ar flux at 773 K during 2 h. Subsequently, the gas was switched to a mixture with a water-to-ethanol molar ratio of 5 during 3 h. The Raman spectra were taken every 20 min.
- The samples were cooled down in Ar after 3 h under reaction conditions. Then, the catalysts were exposed to a mixture of 3% O_2 in Ar at increasing temperatures. The Raman spectra were taken every 50 K from 300 K to 823 K.

Similar oxidation experiments were performed on the catalysts used in the fixed-bed reactor during 25 h.

2.4.6. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images were obtained using a Philips CM200 UT transmission electron microscope operated at 200 kV and room temperature. Samples were dispersed onto a lacey carbon grid without ultrasonic dispersion.

3. Results and discussion

3.1. Characterization of calcined and reduced catalysts

The diffraction patterns obtained for the supports (not shown) and the calcined $\text{Rh}/\text{La}_2\text{O}_3(x)\text{-SiO}_2$ catalysts (Fig. 1) mainly exhibit the broad signal related to the amorphous SiO_2 . In addition, a shoulder at about $2\theta = 29^\circ$ and small broad reflections at $2\theta = 45^\circ$ are observed; these are symptomatic of the presence of lanthanum disilicate ($\text{La}_2\text{Si}_2\text{O}_7$) since these reflections coincide with the main peaks given for this compound (JCPDS No. 21-1014) [17,26]. Kepiński et al. [27] reported an XRD study of the crystallinity of binary $\text{La}_2\text{O}_3\text{-SiO}_2$ composites. According to these

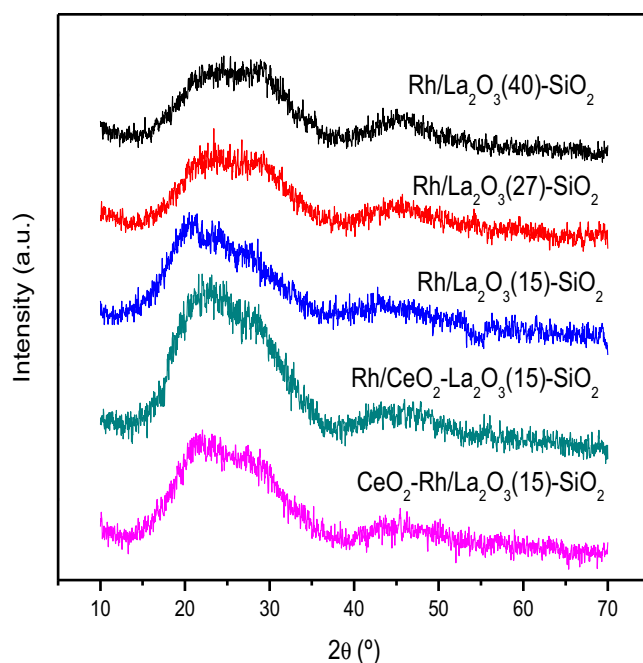


Fig. 1. XRD patterns of fresh catalysts.

authors, the composite remains amorphous up to a calcination temperature of 1223 K, which is consistent with the diffraction patterns reported in the present work since the calcination temperature was 823 K. No diffraction peaks of cerium oxides were observed in the $\text{Rh}/\text{CeO}_2\text{-La}_2\text{O}_3(15)\text{-SiO}_2$ and the $\text{CeO}_2\text{-Rh}/\text{La}_2\text{O}_3(15)\text{-SiO}_2$ catalysts (Fig. 1) and supports (not shown) that contained Ce.

In a previous study, we characterized [28] the binary $\text{La}_2\text{O}_3\text{-SiO}_2$ supports through several techniques such as XRD, Ion scattering spectroscopy (ISS) and XPS. The results suggested the formation of a uniform layer of lanthanum disilicate over $\text{La}_2\text{O}_3\text{-SiO}_2$ supports with 40% of lanthanum oxide. For a La_2O_3 content lower than 40% the layer formed was not high enough to cover the entire support surface. Meanwhile, for higher contents of lanthanum, LaO_x surface segregation occurred. These supports were employed for the preparation of Ru catalysts. We found that the interaction between the Ru metal and the support increased with the lanthanum content up to 27% of lanthanum oxide.

The reduced Rh catalysts were characterized through XPS. The binding energy (BE) and full width at half maximum (FWHM) for Rh $3d_{5/2}$ and La $3d_{5/2}$ core levels are listed in Table 1. According to the literature [29], for the Rh^0 species the main peak should appear in the range between 307.0 and 307.5 eV, at about 308.1 eV for Rh^{+1} and between 308.3 and 310.5 eV for Rh^{+3} . In our catalysts, the binding energy values were close to $306.9 \pm 0.2 \text{ eV}$ for all catalysts, thus confirming that the rhodium particles were completely reduced at the surface.

For the lanthanum species, the binding energies and the main peak–satellite splits are close to 3.7 eV in agreement with those previously reported [28] for $\text{Ru}/\text{La}_2\text{O}_3\text{-SiO}_2$ catalysts. In this previous work, we compared the La 3d spectra of catalysts and supports with the one in the pure lanthanum sample. Similar binding energies were observed. Nevertheless, a difference in the main peak to satellite (shake up) peak intensity ratio was observed and could be assigned to the possible formation of a well-dispersed lanthanum disilicate phase on the support surface. In the case of Rh catalysts, by increasing the amount of lanthanum at the support, the surface atomic concentration of La also increased. The lowest surface concentration of rhodium (Table 1) was obtained for $\text{Rh}/\text{La}_2\text{O}_3(15)\text{-SiO}_2$.

Table 2

Metallic dispersion and particle size of reduced catalysts estimated by XPS, applying the Davis model, and by CO chemisorption.

Catalyst	Dispersion (%)		Particle size (nm)	
	Chemisorption	XPS	Chemisorption	XPS
Rh/La ₂ O ₃ (15)–SiO ₂	29	43	3.7	2.5
Rh/La ₂ O ₃ (27)–SiO ₂	81	77	1.3	1.4
Rh/La ₂ O ₃ (40)–SiO ₂	79	63	1.4	1.7
Rh/CeO ₂ –La ₂ O ₃ (15)–SiO ₂	87	89	1.2	1.2

The Ce 3d region of the XPS spectrum (not shown) for the reduced catalysts Rh/CeO₂–La₂O₃(15)–SiO₂ and CeO₂–Rh/La₂O₃(15)–SiO₂ showed the absence of the peak at 916.5 eV which, according to the literature [30], is symptomatic of the presence of Ce⁴⁺; suggesting that cerium at the surface was present as a reduced Ce³⁺ species. In the calcined solid, the Ce 3d regions showed a low intensity peak at 916.5 eV. From its intensity we were able to estimate the proportion of Ce³⁺; this value was equal to 24%. The Ce surface atomic concentration was similar in both samples, 0.65% for Rh/CeO₂–La₂O₃(15)–SiO₂ and 0.51% for the CeO₂–Rh/La₂O₃(15)–SiO₂ catalyst.

In addition to the surface composition and chemical state information, the XPS technique could be used to estimate particle size by applying different models [31]. In order to perform an estimation of the Rh⁰ particle size of the Rh/CeO₂(y)–La₂O₃(x)–SiO₂ catalysts studied in this work, the Davis model was applied [24].

The Rh particle sizes are summarized in Table 2, the values being within the 1.2–2.5 nm range. The metal dispersion was also determined by static CO chemisorption (Table 2). Both techniques predicted the same trend for the metallic dispersion and particle size for all catalysts. Nevertheless, a significant deviation was observed for the biggest particle size, in which a value of 2.5 nm was obtained by XPS and 3.7 nm by CO chemisorption. Recently, Wojcieszak et al. [32] successfully applied this model for the characterization of Pd nanoparticles synthesized by the water-in-oil microemulsion method using TiO₂ as support. These authors found that the Davis model seemed to be adequate to determine the size of small and big Pd particles as compared with other methods [32]. However, to the best of our knowledge, it was not previously applied for Rh nanoparticles. The results supported that XPS analysis could be a useful tool in the characterization of small metallic particles.

Mattos et al. [22] reported that the ethanol steam reforming requires a smaller quantity of metallic atoms assembled than the carbon formation reactions, so that smaller metal particles would lead catalysts with higher carbon formation resistance. As stated above, the particle size determined for each catalyst was in the range between 1.2 and 3.7 nm. This could lead to a high carbon formation resistance. On the other hand, at the reaction conditions employed, high temperature and a slightly reductive environment, the metallic sintering could be favored.

As observed in Table 2, the cerium addition to the catalysts increased the metallic dispersion from 29 to about 87%. A similar effect was reported on Rh/CeO₂–Al₂O₃ catalysts, where Ce addition to the support inhibited Rh oxidation and particle sintering due to the interaction of the promoting oxide with the active phase [33].

3.2. Activity and stability for the steam reforming of ethanol

Ethanol steam reforming reaction was performed at 773 K, with a W/F of 4.9×10^{-3} g h L⁻¹ and by feeding two different water to ethanol molar ratios (3 and 5). Table 3 shows the product distribution after 2 h on stream; at that time, all catalysts showed a 100% of ethanol conversion except for the catalyst with 40% of La₂O₃ with R=3. The equilibrium composition of the products under the

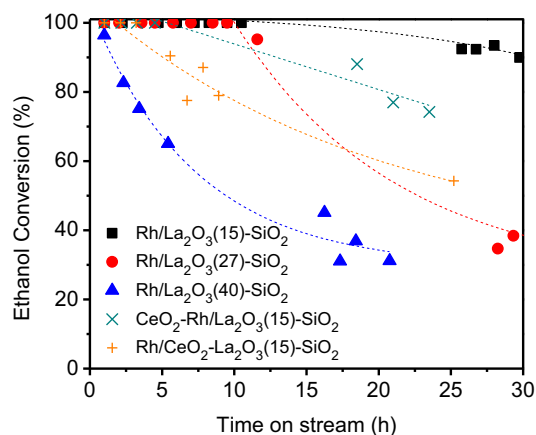


Fig. 2. Ethanol conversion as a function of time on stream. $R=3$ M, $T_R=773$ K, $W/F: 4.9 \times 10^{-3}$ g h L⁻¹, $y_{\text{EtOH}}=0.025$.

same conditions, determined by Gibbs free energy minimization, was added as a reference to the activity level of the catalysts. As observed in Table 3, all catalysts showed a high activity for the ethanol steam reforming reaching product compositions similar to the equilibrium ones. The highest differences between thermodynamic and experimental values were observed for hydrogen and methane compositions with a water to ethanol molar ratio of 5. This could be an indicator of a low activity for the methane steam reforming of the evaluated catalysts at 773 K. Neither was ethylene detected under these reaction conditions nor acetaldehyde at the reactor outlet when the ethanol conversion was 100%.

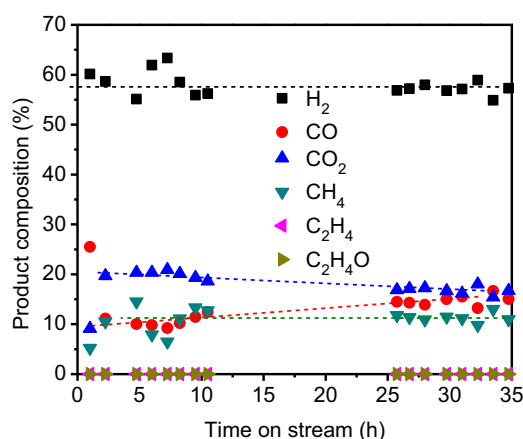
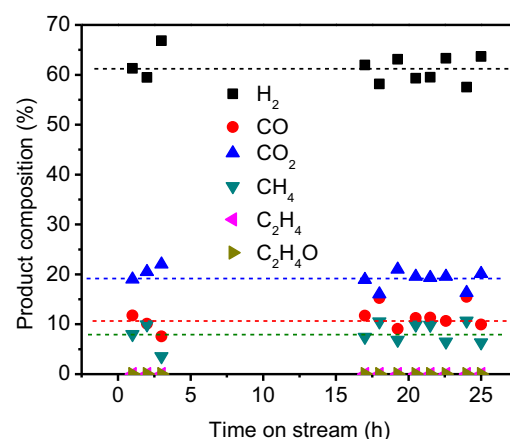
The Rh/La₂O₃(40)–SiO₂ catalyst was the only catalyst that produced acetaldehyde from the very beginning (1.0% at 2 h) for a steam to ethanol molar ratio equal to 3; as mentioned above, the ethanol conversion over this sample at 2 h was lower than 100% (84%).

In order to study the catalyst stability, the catalysts were tested during 25 h. Ethanol conversions as a function of reaction time, at 773 K and a water to ethanol molar ratio of 3 are shown in Fig. 2. All catalysts showed deactivation with time-on-stream; the catalyst with 27 and 40% of La₂O₃ showed the strongest deactivation, about 70% after 20 h of reaction. The Rh/La₂O₃(15)–SiO₂, CeO₂–Rh/La₂O₃(15)–SiO₂ and Rh/CeO₂–La₂O₃(15)–SiO₂ catalysts presented an ethanol conversion of about 90%, 75% and 55%, respectively, after 25 h of reaction. The reaction product distribution with $R=3$ is shown in Fig. 3 for the Rh/La₂O₃(15)–SiO₂ catalyst. In all catalysts, the percentage of carbon monoxide increased with the reaction time, while the carbon dioxide decreased; this could be an indicator of a progressive deactivation, in which the catalysts gradually lost their activity for the water gas shift reaction. In addition, the catalysts with 15% p/p of lanthanum oxide in their support showed about the same composition of both carbon monoxide and carbon dioxide after 25 h on reaction conditions. In the catalysts with higher La₂O₃ content, the molar fraction of CO almost doubled that of the CO₂ fraction (not shown), suggesting a stronger decrease in water gas shift activity when the percentage of La increased. With the exception of Rh/La₂O₃(15)–SiO₂, all catalysts produced acetaldehyde after 20 h on stream (not shown). At this low steam to ethanol ratio (Fig. 2), the catalysts with Ce deactivated before the one without cerium.

With a steam to ethanol ratio of 5 (Fig. 4), all catalysts showed an initial ethanol conversion of 100%. The CeO₂–Rh/La₂O₃(15)–SiO₂ catalyst suffered deactivation from the beginning of the reaction (about 2 h), and the catalysts with lanthanum oxide content higher than 15% showed a progressive deactivation from hour 18 of reaction, following the same trend. On the other

Table 3Product compositions after 2 h on stream. $T_R = 773$ K, $W/F = 4.9 \times 10^{-3}$ g h L $^{-1}$.

Catalyst	R^a	H ₂	CO	CO ₂	CH ₄	C ₂ H ₄ O
Equilibrium ^b	3	62.5	8.0	19.0	10.5	0.0
	5	68.2	5.7	20.7	5.33	0.0
Rh/La ₂ O ₃ (15)–SiO ₂	3	58.7	11.1	19.7	10.5	0.0
	5	58.0	9.4	20.4	12.2	0.0
Rh/La ₂ O ₃ (27)–SiO ₂	3	58.1	10.7	20.0	11.2	0.0
	5	59.0	10.4	20.7	9.9	0.0
Rh/La ₂ O ₃ (40)–SiO ₂	3	57.7	12.3	18.0	11.0	1.0
	5	68.0	7.1	22.4	2.5	0.0
CeO ₂ –Rh/La ₂ O ₃ (15)–SiO ₂	3	57.6	15.0	16.5	10.9	0.0
	5	60.2	11.7	19.2	8.9	0.0
Rh/CeO ₂ –La ₂ O ₃ (15)–SiO ₂	3	54.8	15.1	16.7	13.5	0.0
	5	64.0	7.2	22.9	5.9	0.0

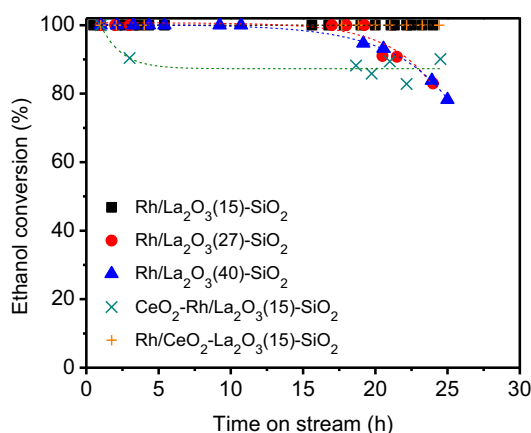
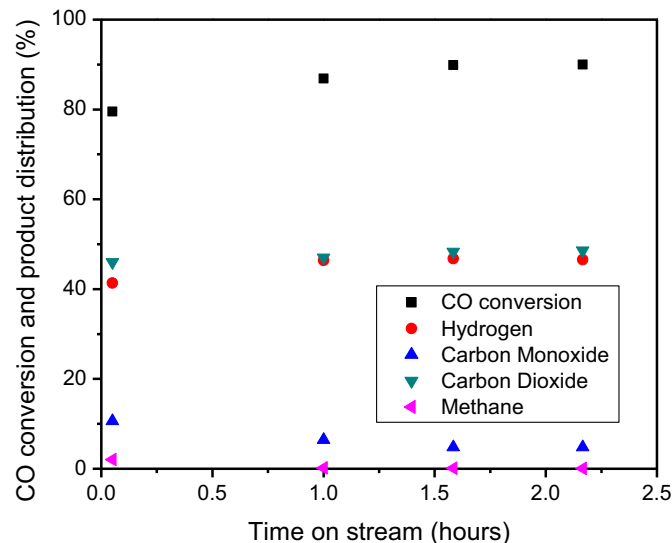
^a Steam to ethanol molar ratio.^b Thermodynamic equilibrium compositions were calculated by Gibbs free energy minimization using COCO simulator software [19].**Fig. 3.** Product composition as a function of time on stream, for the catalyst Rh/La₂O₃(15)–SiO₂. $R = 3$ M, $T_R = 773$ K, $W/F: 4.9 \times 10^{-3}$ g h L $^{-1}$, $y_{\text{EtOH}} = 0.025$.**Fig. 5.** Product composition as a function of time on stream, for the catalyst Rh/La₂O₃(15)–SiO₂. $R = 5$ M, $T_R = 773$ K, $W/F: 4.9 \times 10^{-3}$ g h L $^{-1}$, $y_{\text{EtOH}} = 0.02$.

hand, the Rh/La₂O₃(15)–SiO₂ catalyst held an ethanol conversion of 100% during 25 h. The same behavior was observed for the catalyst with cerium impregnated on the binary support (Rh/CeO₂–La₂O₃(15)–SiO₂). Despite the fact that the addition of cerium to the catalysts increased the metallic dispersion (Table 2) from 29 to about 87%, there was no difference in the catalyst stability at high steam to ethanol ratio.

The product distribution is shown in Fig. 5 for the Rh/La₂O₃(15)–SiO₂ catalyst under the same conditions of Fig. 4. The H₂ composition of the reactor outlet suggests that the catalyst

was selective for hydrogen production and both CO and CO₂ concentrations remained constant with time-on-stream.

When stability tests are carried out at 100% of ethanol conversion, the water to ethanol molar ratio plays a key role; higher values should lead to higher stabilities. The increase in water to

**Fig. 4.** Ethanol conversion as a function of time on stream. $R = 5$ M, $T_R = 773$ K, $W/F: 4.9 \times 10^{-3}$ g h L $^{-1}$, $y_{\text{EtOH}} = 0.02$.**Fig. 6.** Water gas shift reaction over Rh/La₂O₃(15)–SiO₂ catalyst. Reaction temperature: 773 K, $W/F: 4.9 \times 10^{-3}$ g h L $^{-1}$, CO 5% v/v, H₂O to CO molar ratio of 4 and a total gas flow (including Ar as inert) of 68 mL min $^{-1}$.

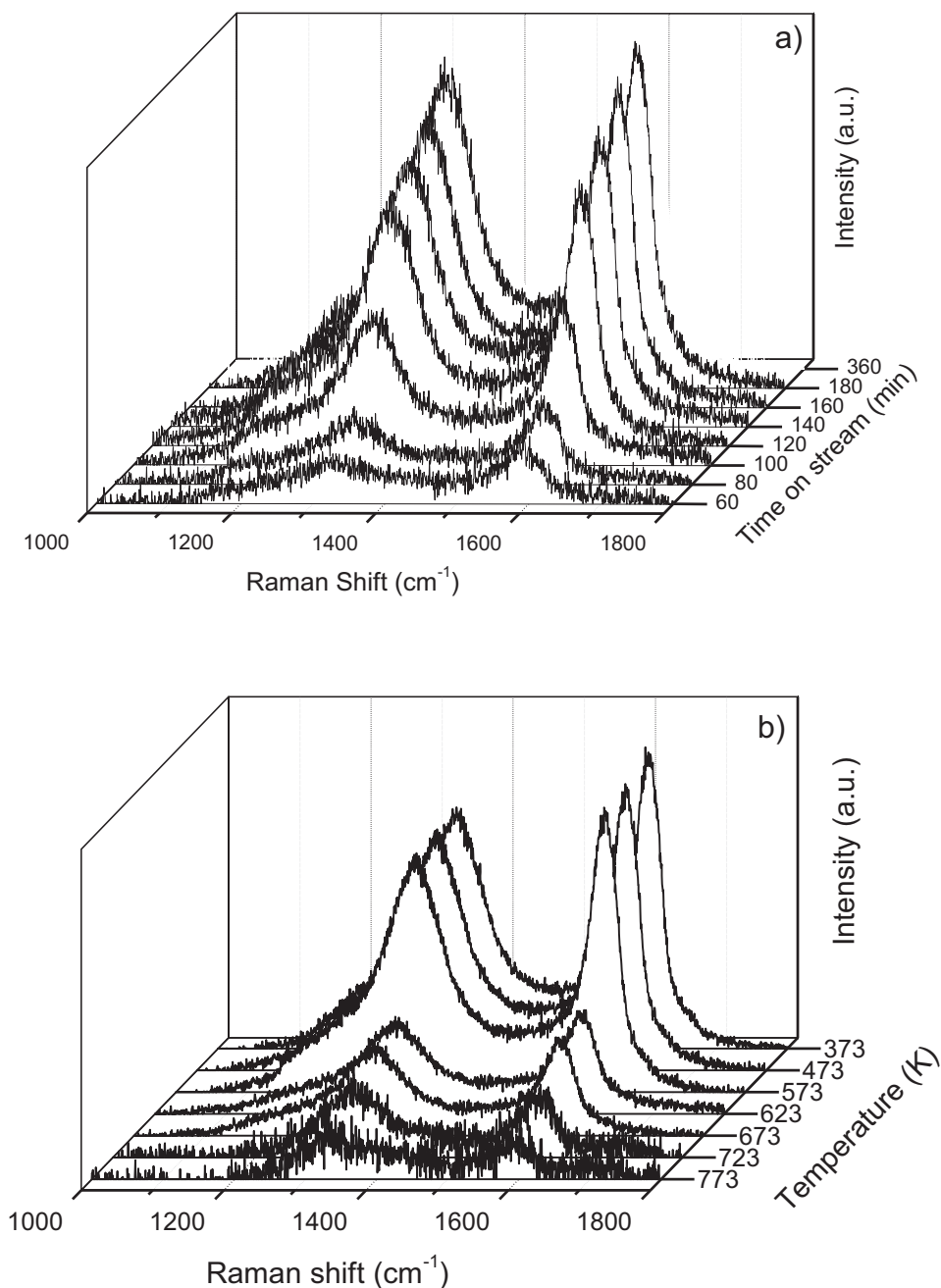


Fig. 7. In situ laser Raman spectroscopy studies: (a) ethanol steam reforming over Rh/La₂O₃(15)–SiO₂ at 773 K with $R=5$; (b) the samples were cooled down to 300 K, and then a mixture of 3% O₂/Ar was fed at increasing temperatures.

ethanol ratio has two main advantages; first, a high amount of water displaces the methane steam reforming and the water gas shift reactions to the products increasing the hydrogen production [11]. Second, the presence of water inhibits the ethylene production and can also produce carbon gasification, leading to a reduction in the amount of carbon deposited over the catalysts [22]. On the other hand, a high steam composition at the feed also implies a high amount of energy for water vaporization; as a consequence, the energy efficiency of the overall process decreases. Francesconi and co-workers [34] studied the efficiency of the complete ethanol steam reforming system, including hydrogen purification and the PEM fuel cell, and they concluded that the optimum value for the water to ethanol molar ratio is between 4 and 5. With this ratio and at a reaction temperature of 773 K, the Rh/La₂O₃(15)–SiO₂

catalyst was stable during 25 h. It was in the same order as that of the Rh/CeO₂ catalyst with high surface area reported by da Silva et al. [11]. The hydrogen production was also similar to that reported for the Rh/CeO₂ catalyst.

Chen et al. reported that by the addition of Fe_xO_y to the Rh(1)/Ca–Al₂O₃ catalyst [35], they enhanced the water gas shift activity of the catalyst leading to a CO-free product current and a high increase in terms of catalyst stability on ethanol steam reforming, from 10 to 300 h on stream. Rh supported on La₂O₃(27)SiO₂ has also been reported [36] as an active catalyst for the water gas shift reaction at 723 K. In addition, the catalytic activity for the water gas shift reaction of Rh/La₂O₃(15)–SiO₂ was measured at 773 K, reaching a CO conversion equal to 89%, with a H₂/CO₂ ratio close to 1 (Fig. 6).

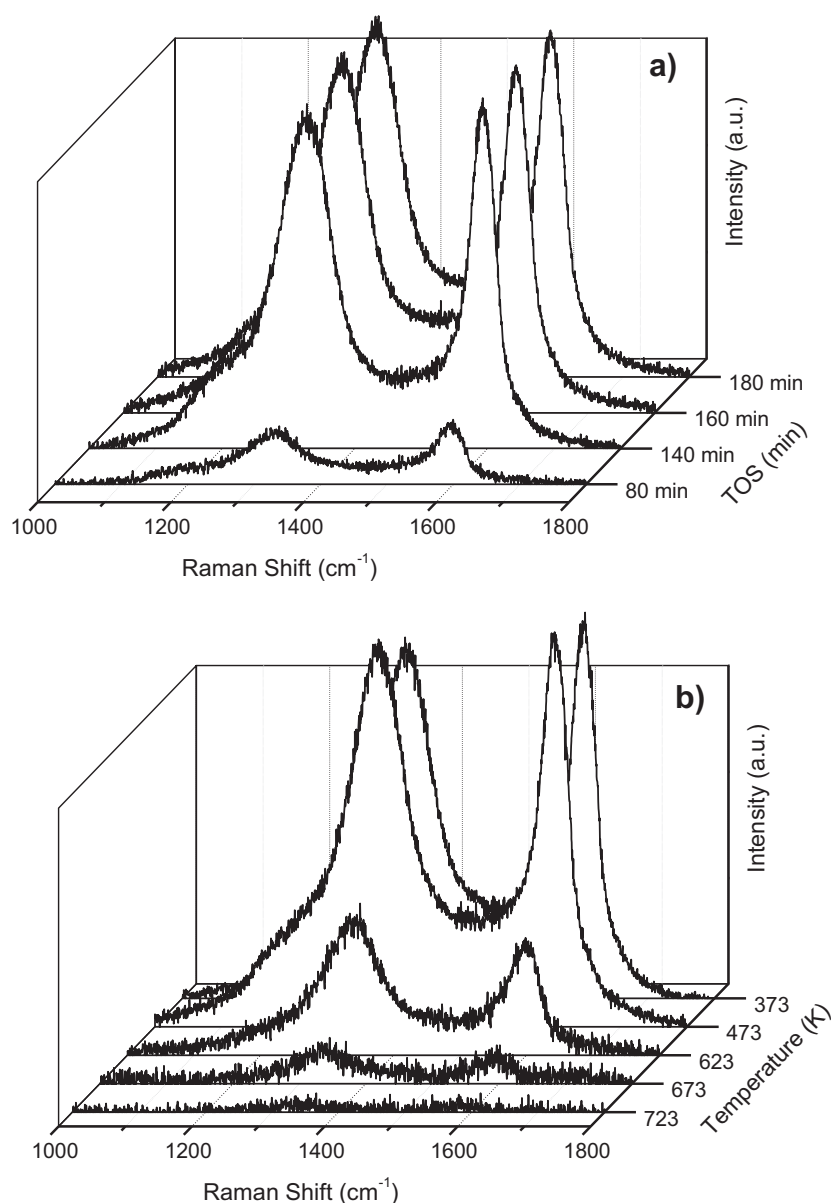


Fig. 8. In situ laser Raman spectroscopy studies: (a) ethanol steam reforming over Rh/La₂O₃(40)–SiO₂ at 773 K with $R=5$; (b) the samples were cooled down to 300 K, and then a mixture of 3% O₂/Ar was fed at increasing temperatures.

3.3. Carbon deposition and deactivation of Rh catalysts

In order to study the evolution of the carbon species under reaction conditions, in situ Raman spectroscopy measurements were performed, since this technique is very sensitive to the presence of carbon deposits. In the case of hexagonal crystal graphite, the Raman spectra consisted of the main first order band (G band) assigned to the in plane displacement of carbon atoms in the hexagonal sheets [37]. When disorder was introduced into the graphite structure, the existing bands broadened and additional bands were found at about 1350 cm⁻¹ (D) and 1620 cm⁻¹ (D'). In the rather small or disordered crystal with a very little three-dimensional order, the G and D' bands merged into a single broader feature. For the in situ experiments, the catalyst was loaded into a cell coupled to the spectrometer. A water to ethanol molar ratio of 5 was used in the feed. In the case of the most stable catalyst (Rh/La₂O₃(15)–SiO₂), a slow carbon formation could be observed during the first hour of reaction, showing an increase with the reaction time (Fig. 7a). For catalyst (Rh/La₂O₃(40)–SiO₂), carbon

formation was also observed at the beginning of the reaction (Fig. 8a); however, the intensity of the carbon signals was about three times higher than the intensity obtained with the sample with 15% of La₂O₃.

Since carbon signals appeared in the Raman spectra, scanning electron microscopy (SEM) was performed over the used catalysts. However, it was not possible to detect the carbon deposits. When a conventional TPO analysis was carried out on a Rh/La₂O₃(15)–SiO₂ used catalyst the amount of carbon dioxide produced during the temperature-programmed oxidation was lower than the detection limit (1.5 μmol) of the mass-spectrometer used for the determination. This result suggests that the amount of carbon deposited over the catalyst was very low (lower than 3.75×10^{-5} g_c (g_{cat} h)⁻¹). On the other hand, catalyst Rh/La₂O₃(40)–SiO₂ showed an oxidation signal centered at about 723 K and a carbon deposit to catalyst mass ratio of 2×10^{-4} g_c (g_{cat} h)⁻¹.

In order to estimate the type of carbon deposits produced under reaction conditions, carbon oxidation experiments were carried out using the same Raman cell. After the in situ reaction, the samples

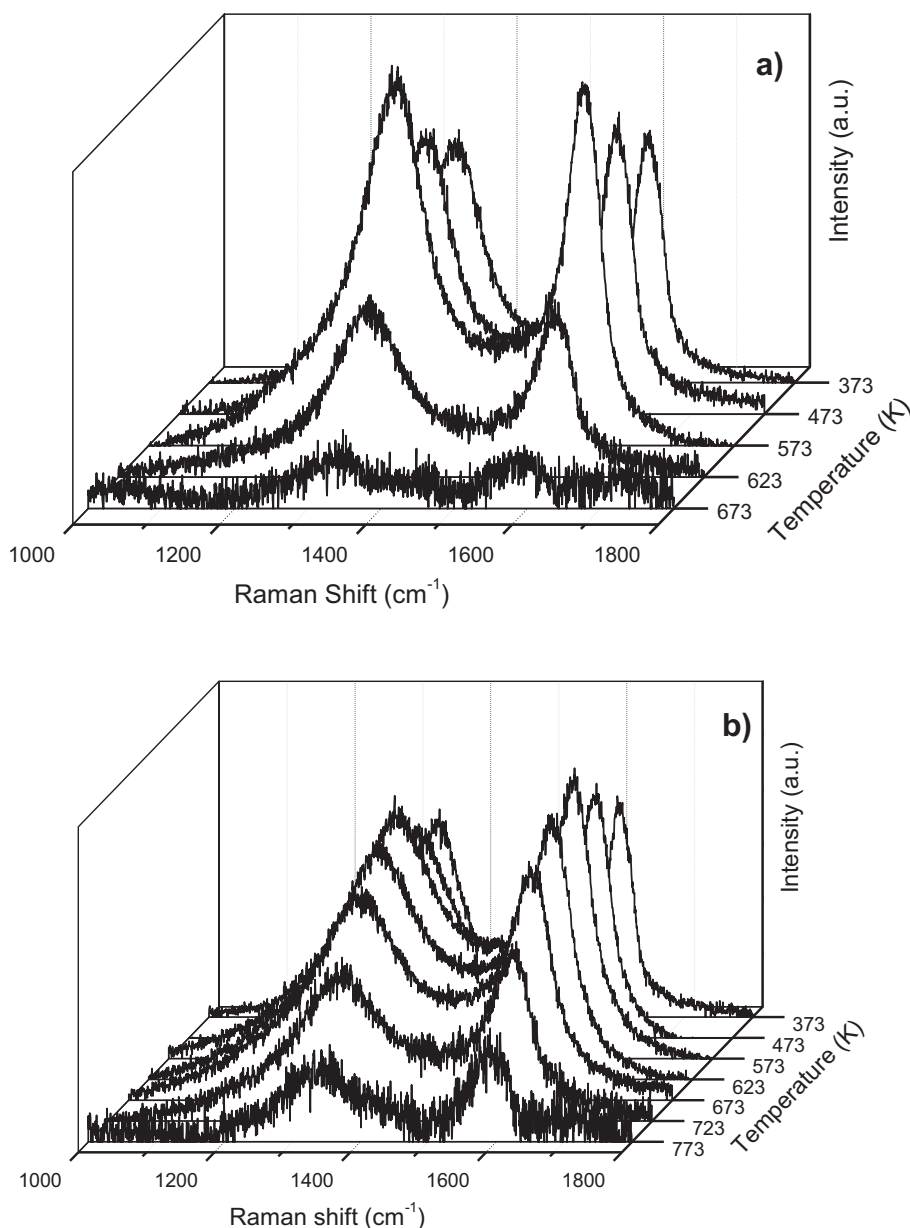


Fig. 9. (a) Rh/La₂O₃(15%)-SiO₂ and (b) Rh/La₂O₃(40%)-SiO₂ both used in the fixed-bed reactor during 24 h in the ethanol steam reforming with $R=5$.

were cooled in an Ar stream and then heated up to 773 K in a O₂(3%)/Ar stream. As shown in Fig. 8b, for the sample with 40% of La₂O₃, the carbon was oxidized between 573 K and 673 K. The same behavior was observed for the Rh/La₂O₃(15%)-SiO₂ catalyst (Fig. 7b).

Mirodatos and coworkers [38] studied the ethanol steam reforming reaction at 773 K using Ir/CeO₂ as catalyst. From TPO experiments, the authors reported two domains of CO₂ which could be related to different types of carbon deposits: during the first 5 h, the carbonaceous deposits formed under reaction conditions were highly reactive species, oxidized at low temperature (between 560 and 570 K) in agreement with the low oxidation temperature (between 573 K and 673 K) observed in our catalysts (Figs. 7b and 8b).

The authors reported a significant accumulation of carbonaceous deposits for longer reaction times, causing the encapsulation of the Ir particles and the support surface. This type of carbon deposits was oxidized at higher temperature (around 800 K); therefore, the latter species were related to the deactivation of the catalysts.

Fig. 9a and b shows the Raman spectra of the in situ oxidation performed over the catalysts with 15 and 40 wt.% of lanthanum oxide used in the fixed-bed reactor during 25 h. Note that in the used catalysts exposed to air after reaction, an increase in the carbon intensity was observed at 573 K. This could be due to the release of adsorbed species, increasing the signal intensity of graphitic carbon.

It can be seen (Fig. 9a) that the carbonaceous deposits on the Rh/La₂O₃(15%)-SiO₂ catalyst were oxidized at the same temperature as the system evaluated for only 3 h using the in situ Raman cell. On the other hand, for the Rh/La₂O₃(40%)-SiO₂ catalyst (Fig. 9a) the carbon deposits were oxidized at higher temperature (773–823 K), in agreement with the oxidation temperature observed in the conventional TPO experiment and with the results obtained by Mirodatos and coworkers [38] on an Ir/CeO₂ catalyst. They observed that the encapsulation carbon related to the catalyst deactivation was burnt out at higher temperature.

For all used catalysts, the Raman spectra only showed the D and G peaks. The G and D' bands seemed to merge in one peak,

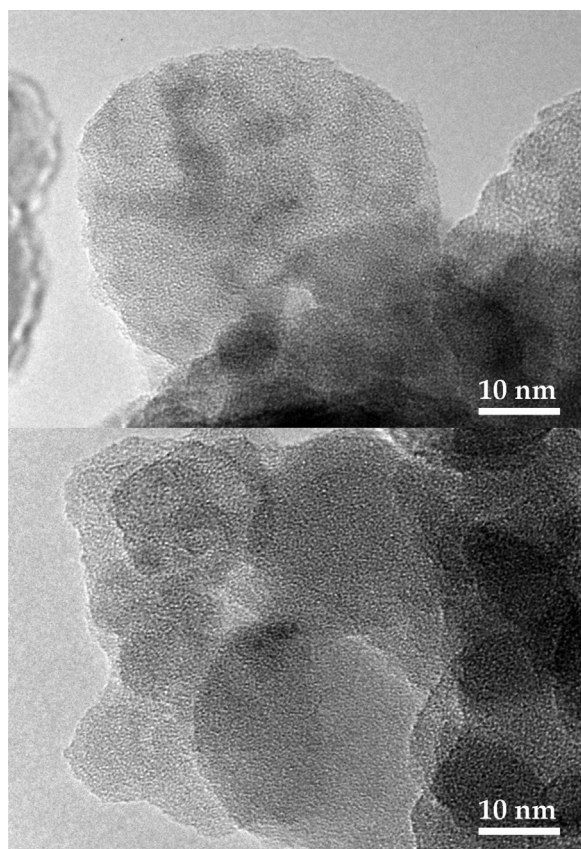


Fig. 10. TEM images of Rh/La₂O₃(15)–SiO₂ catalyst after reduction at 773 K during 2 h.

suggesting the presence of disordered graphitic carbon with small three-dimensional order [39].

In addition, we performed TEM studies in order to obtain direct information about the formation and distribution of carbon deposits with high spatial resolution. Fig. 10 shows images of the unreacted catalysts after reduction. A contrast is observed, typical of amorphous materials, consistent with the XRD results. This contrast makes it more difficult to detect the formation of carbonaceous material. In consequence, an unambiguous identification has to proceed by carefully studying the edges of the crystals constituting the support. It has to be considered that the edges of the crystals do not show any additional feature.

Fig. 11 shows TEM images of the Rh/La₂O₃(15)–SiO₂ catalyst after 24 h of reaction. The upper image shows the formation of a disordered structure on the left side which we attributed to disordered graphitic carbon because the average lattice fringe measured is around 3.5 Å. Interestingly, this kind of deposit is present in other areas of the particle but its distribution is not uniform over its surface. This observation is clearly appreciated by looking at the crystal edge. In the lower image we can appreciate that the surface does not seem to be covered by any carbon material. These observations are consistent with the activity shown by this catalyst after 24 h of reaction.

Fig. 12 shows images corresponding to the Rh/La₂O₃(40)–SiO₂ catalyst. In the upper image we can observe the formation of the graphitic disordered deposits. A careful inspection allows one to distinguish the distinctive contrast due to amorphous carbon as a more continuous covering of the support. Although visible in the image, the formation of this amorphous carbon layer can be better observed in situ as a function of the defocus in the microscope. This layer has a variable thickness over the same crystal as shown in the lower image. The formation of this layer is

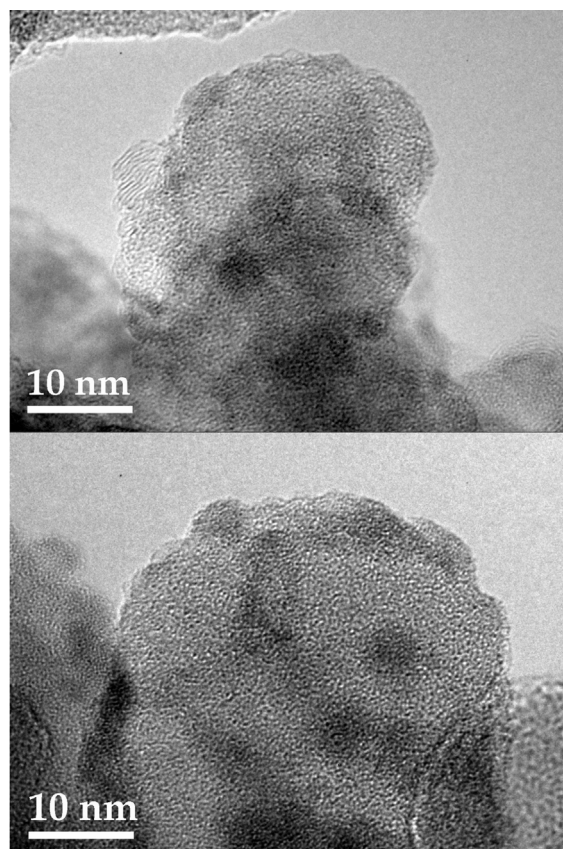


Fig. 11. TEM images of the Rh/La₂O₃(15)–SiO₂ catalyst used during 24 h in the steam reforming of ethanol at 773 K, with a water to ethanol molar ratio of 5 and a space velocity of $4.9 \times 10^{-3} \text{ g h L}^{-1}$.

consistent with the partial deactivation observed in this sample. TEM results are in agreement with the oxidation experiments of the carbonaceous deposits followed by Raman spectroscopy. The catalyst with 15 wt.% of La₂O₃ showed low oxidation temperatures indicating that the particles are not fully covered by carbon, while Rh/La₂O₃(40)–SiO₂ seems to be covered by a continuous carbon layer due to the higher temperatures required for its complete oxidation.

In order to understand the role of the support on the stability of the solids and, consequently, on the carbon formation, DRIFTS experiments were performed at 773 K during 2 h under reaction conditions (Fig. 13). After 10 min on stream, the presence of a band at 2020 cm^{-1} assigned to linearly adsorbed CO on Rh [40], and bands in the $2900\text{--}2980 \text{ cm}^{-1}$ region due to CH_x species were observed in both catalysts. These bands could be related to the formation of CO from the direct decomposition of ethoxy species or indirect decomposition of acetaldehyde and/or acetyl intermediates. Noronha and coworkers [11,40] studied the mechanism of the catalyst deactivation for steam reforming of ethanol reaction over Pt/CeZrO₂ and Rh/CeO₂ catalysts using DRIFTS experiments carried out under reaction conditions. The authors proposed a reaction mechanism where the ethanol adsorbs dissociatively to form ethoxy species on the surface. The ethoxy species is dehydrogenated to acetaldehyde and acetyl, which may be further oxidized to acetate. Note that a water to ethanol ratio of 2 was employed. In our case, with a water to ethanol ratio equal to 5, no bands assigned to acetate species or carbonates were observed due to the decomposition of the adsorbed species promoted by the excess of water [40]. In addition, acetaldehyde formation was not observed in the stability experiments (Fig. 5). Therefore, direct decomposition

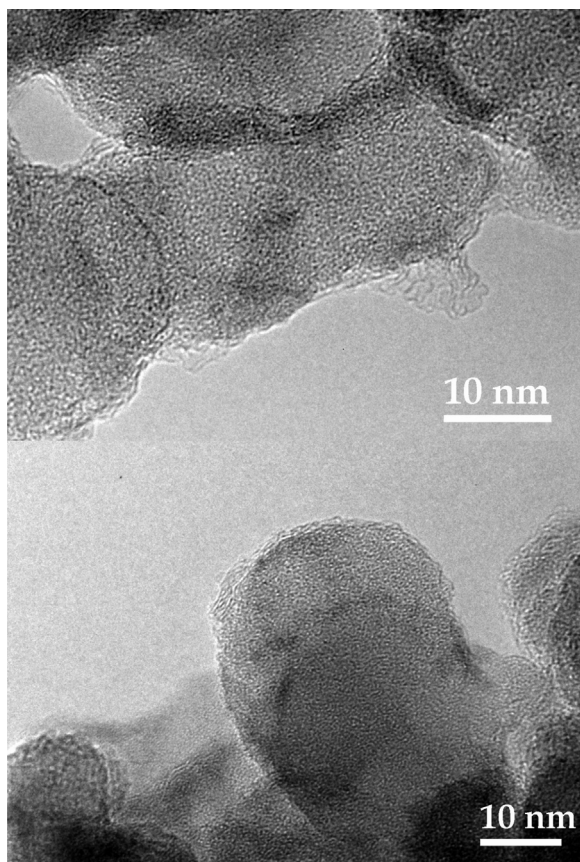


Fig. 12. TEM images of the Rh/La₂O₃(40)–SiO₂ catalyst used during 24 h in the steam reforming of ethanol at 773 K, with a water to ethanol molar ratio of 5 and a space velocity of $4.9 \times 10^{-3} \text{ g h L}^{-1}$.

of ethoxy species would produce hydrogen, CO, and CH_x species, which could result in carbon formation.

da Silva et al. [11] reported an accumulation of CH_x species due to an unbalance between the rate of decomposition of dehydrogenated and acetate species to H₂, CO, and CH_x species and the rate of desorption of the CH_x species as CH₄. They sustained that this CH_x species may be further dehydrogenated leading to the accumulation of carbon deposits and obstruction of the Rh-support interface, resulting in catalyst deactivation. They claimed that the catalyst deactivation depends on the reforming activity of the metal at the reaction temperature.

In brief, by DRIFTS experiments it was only possible to discuss the mechanism of carbon formation on Rh/La₂O₃–SiO₂. However, no difference between both catalysts was observed that would allow us to explain which is the role of the La₂O₃ content on carbon formation and catalyst stability.

In the literature, the deactivation of the catalyst has been correlated to the sintering of the metal particles [22]. The support can also contribute to the stabilization of metal particles at high temperatures in the presence of steam. In the case of CeO₂ containing supports, the metal–ceria interaction was proposed as preventing the growth of highly dispersed metal particles during steam reforming of ethanol at high temperatures. Thus, the metal–support interfacial area was kept relatively constant, maintaining the stability of the catalysts.

The encapsulation of metal particles by a reducible support, like CeO₂ or La₂O₃, was also considered as a factor that can cause a buildup of acetate species on the surface leading to catalyst deactivation. However, in the case of Pt/CeZrO₂ catalysts the decoration of metal particles during the ethanol steam reforming has been ruled out [40].

The sintering of Rh metal particles during reaction was studied by XPS. However, Rh 3d peaks were not detected in the catalysts used during 25 h. This could be due to carbon deposits that cover

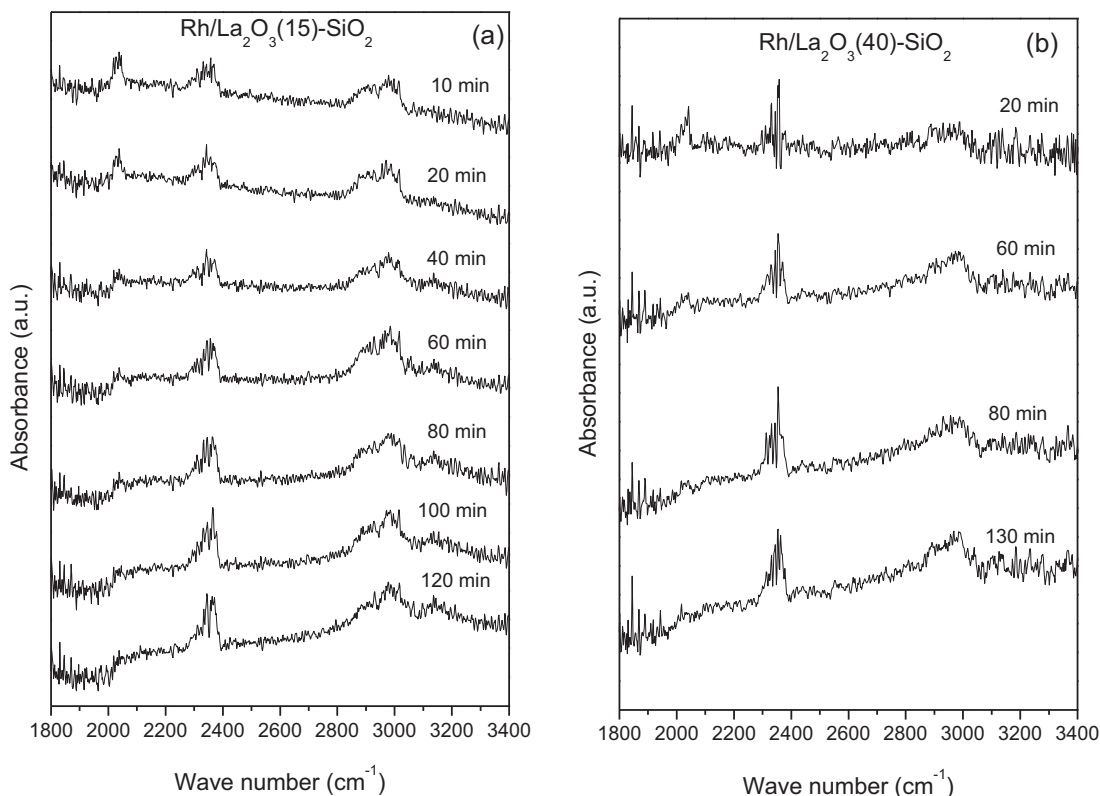


Fig. 13. In situ DRIFTS spectra of ethanol steam reforming at 773 K over (a) Rh/La₂O₃(15)–SiO₂ and (b) Rh/La₂O₃(40)–SiO₂ catalysts, with water to ethanol molar ratio of 5.

the catalyst surface, increasing the intensity of the C1s peak and the broadening of the high binding energy region.

In the used Rh/CeO₂–La₂O₃(15)–SiO₂ catalyst, the ratio between cerium and lanthanum at the surface observed by XPS remained constant, about 0.3. Meanwhile, in the CeO₂–Rh/La₂O₃(15)–SiO₂ catalyst, this ratio decreased four times in the used catalyst, reaching a very low value of 0.07.

In order to estimate the particle size for the used catalysts, the catalytic samples were exposed to reaction conditions during only 2 h. Then, the samples were characterized through XPS and the results were summarized in Table 1. Note that the Davis model could not be applied because the Auger peak could not be detected. Nevertheless, the surface concentrations and Rh/La surface atomic ratios were calculated.

For the Rh/La₂O₃(15)–SiO₂ catalyst, the Rh/La ratio increased in comparison with the reduced catalysts. However, this ratio remained constant for the Rh/La₂O₃(40)–SiO₂ catalyst. In both cases, the values are higher than the nominal Rh/La ratio. This variation in the Rh/La surface ratio for the used catalysts could be related to the metal support interaction, which could produce the decoration of metal particles leading to catalyst deactivation.

The main difference between the used catalysts was found in the surface oxidation state of Rh. In the former catalyst, the Rh 3d peak appears at 308.4 eV, indicating that Rh⁰ was oxidized to Rh⁺⁺ and for the most stable catalyst, Rh remained in its reduced state.

The oxidation of the metal particle was also proposed as deactivation route during methane steam reforming by Hensen and coworkers [41]. These authors found that the support only affects the catalytic activity indirectly by influencing the Rh dispersion and the reduction degree of the metal phase. The oxidation of the metal could be influenced by particle size effects, with small particles being more easily oxidized. Their catalysts with Rh nanoparticles smaller than 2.5 nm deactivate more strongly than catalysts with larger nanoparticles.

Similarly, when 40% of La₂O₃ was employed in the support, the Rh particles were smaller (1.7 nm) and an oxidation of surface Rh was detected by XPS in the used catalyst, that could be responsible for the highest deactivation and carbon formation observed in this catalyst. In contrast, the catalyst with a lower La₂O₃ content presents the biggest particle size and the highest stability at both steam to ethanol molar ratios, in agreement with the presence of Rh in its reduced oxidation state after being used during 25 h.

The higher stability of the catalyst with low lanthanum oxide concentration could be assigned to the strong interaction between Rh and lanthanum which brings into low dispersion (bigger particle sizes close to 3 nm) which inhibits Rh oxidation under reaction conditions.

4. Conclusions

The ethanol steam reforming reaction was performed at 773 K over Rh/La₂O₃–SiO₂ catalysts employing different La₂O₃ loadings. The catalyst with 15 wt.% of lanthanum oxide was the most stable one at the two different steam to ethanol ratios studied. When the water to ethanol molar ratio was 5, the ethanol conversion was kept at 100% for at least 25 h on stream.

For the fresh catalysts, the metal dispersion and the average particle size of rhodium were determined by applying the XPS Davis model and by CO chemisorption. The results obtained by employing both techniques followed the same trend and confirmed that all catalysts had nanometric metal particles. Despite the fact that the Rh/La₂O₃(15)–SiO₂ catalyst had the biggest particle size, it was the most stable one. By the addition of a low amount of cerium to the catalyst, it was possible to increase the metallic dispersion; however, it did not improve the stability under reaction conditions.

In order to explain the deactivation phenomena, several tests were carried out over the used catalysts. Following the carbon signals by Raman spectroscopy during oxidation at increasing temperatures, different oxidation temperatures were observed. In agreement, TEM results provided a direct visualization of the formation of carbonaceous deposits in the catalysts with different degrees of coverage, being distributed more uniformly in the deactivated catalysts.

DRIFTS experiments under reaction conditions suggested that the direct decomposition of ethoxy species would produce hydrogen, CO, and CH_x species, which could result in carbon formation.

Acknowledgments

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